Processing Methods Established To Fabricate Porous Oxide Ceramic Spheres for Thermal Barrier Coating Applications

As gas turbine technology advances, the demand for efficient engines and emission reduction requires a further increase in operating temperatures, but combustion temperatures are currently limited by the temperature capability of the engine components. The existing thermal barrier coating (TBC) technology does not provide sufficient thermal load reduction at a 3000 °F (1649 °C) operating condition. Advancement in thermal barrier coating technology is needed to meet this aggressive goal.

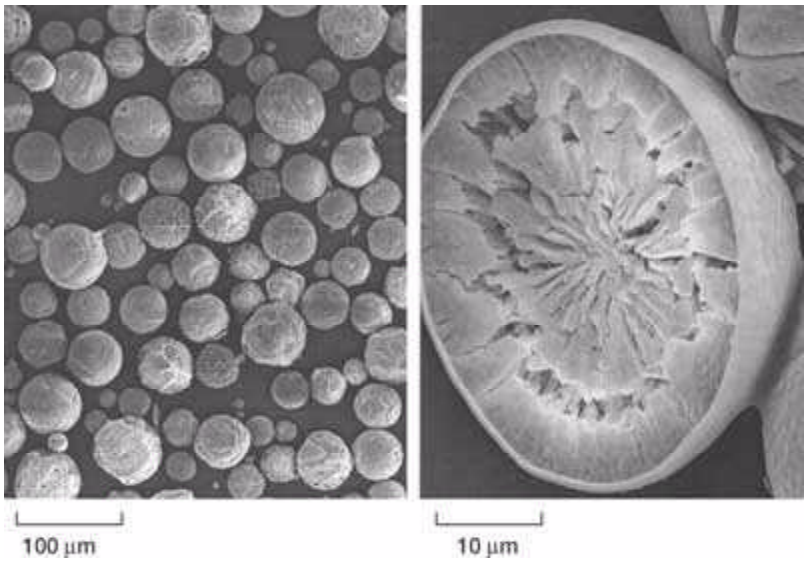
One concept for improving thermal barrier coating effectiveness is to design coating systems that incorporate a layer that reflects or scatters photon radiation. This can be achieved by using porous structures. The refractive index mismatch between the solid and pore, the pore size, and the pore density can be engineered to efficiently scatter photon radiation. Under NASA's Ultra-Efficient Engine Technology (UEET) Program, processing methods to fabricate porous ceramic spheres suitable for scattering photon radiation at elevated temperatures have been established.

A straightforward templating process was developed at the NASA Glenn Research Center that requires no special processing equipment. The template was used to define particle shape, particle size, and pore size. Spherical organic cation exchange resins were used as a structure-directing template. The cation exchange resins have dual template capabilities that can produce different pore architectures. This process can be used to fabricate both metal oxide and metal carbide spheres.

This templating process was used first to fabricate porous zirconia spheres with pore channels. An aqueous solution of a metal salt was used to perform the cation exchange reaction:

$$(ZrO)^{+2} + 2Cl^{-1} + 2(R - SO_3)^{-}H^{+} \leftrightarrow 2\,(R - SO_3)^{-}\,(ZrO)^{+2} + 2\,HCl$$

In this reaction, the hydrogen ion is exchanged with the $(ZrO)^{+2}$ ion. Pyrolyzing the resin beads in an oxidative environment produces metal oxide spheres.

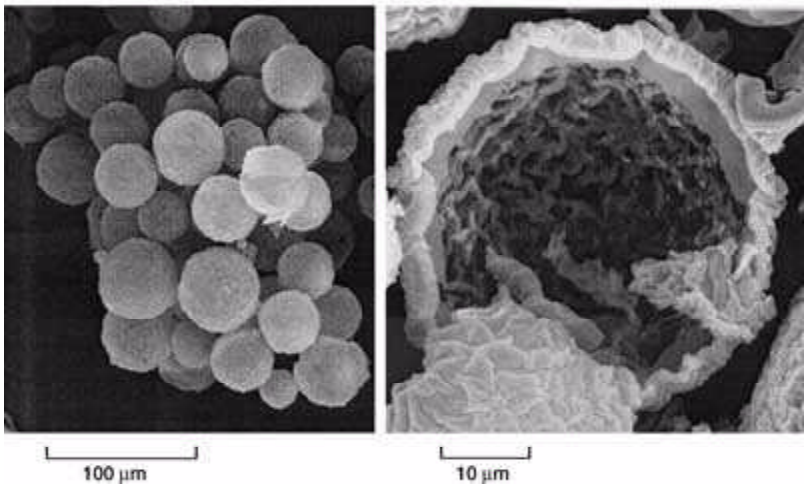


Porous zirconia ceramic spheres with pore channels produced by a cation exchange reaction.

The templating process also was modified to produce hollow spheres. Fabricating hollow spheres allows researchers to explicitly control the size and shape of a pore. A chemical reaction at the resin surface was used to coat the resin particle. Cation exchange resins can retain up to 50 wt% water, which can be utilized to initiate and feed a chemical reaction with metal alkoxides ($M(OR)_n$):

$$Zr(OC_3H_7)_4 + H_2O \text{ <--> } ZrO_2 + 4(C_3H_7OH)$$

The process strategy was an emulsion approach analogous to water in oil. The resin beads were mixed with a nonpolar liquid and surfactant. (Water is immiscible in the nonpolar liquid.) Diluted metal alkoxide solution was prepared by mixing the metal alkoxide with the nonpolar liquid and slowly adding this mixture to the resin bead solution. The chemical reaction deposited a coating on the resin bead surfaces. Pyrolyzing the resin beads in an oxidative environment produced hollow metal oxide spheres. Coating systems are currently being developed using porous and hollow spheres fabricated by the templating process.



Hollow spheres derived by surface templating a strong acid cation exchange resin.

Find out more about this research:
Glenn's Environmental Durability Branch http://www.grc.nasa.gov/WWW/EDB/

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